PERKIN 2

Isolation and characterisation of bis(oxahomo)fullerene derivatives of $C_{60}F_{18}$

Olga V. Boltalina,[a] Benoît de La Vaissière,[b] Andrei Yu. Lukonin,[a] Patrick W. Fowler,[b] Ala'a K. Abdul-Sada,[d] Joan M. Street[c] and Roger Taylor *[d]

[a] *Chemistry Department, Moscow University, Moscow 119899, Russia*
[b] *School of Chemistry, University of Exeter, Stocker Road, Exeter, UK EX4 4QD*
[c] *Chemistry Department, The University, Southampton, UK SO17 1BJ*
[d] *The Chemistry Laboratory, CPES School, Sussex University, Brighton UK BN1 9QJ*

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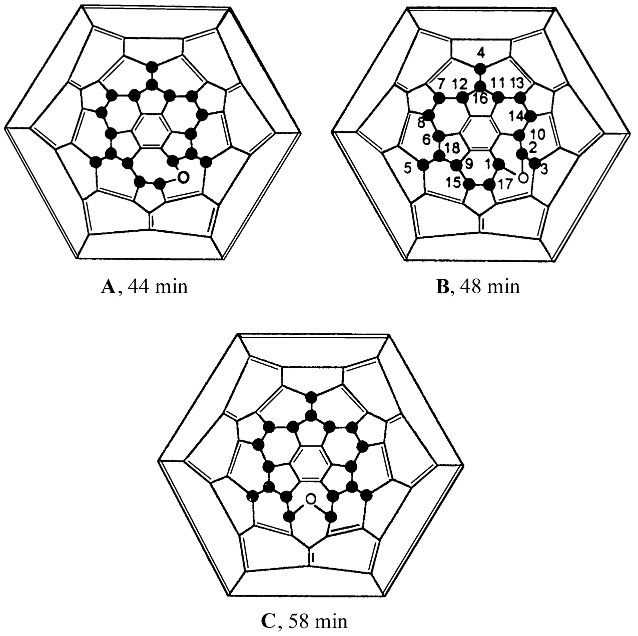
From the products of the reaction of [60]fullerene with K_2PtF_6 under vacuum at 465 °C we have isolated seven isomers of $C_{60}F_{18}O_2$, and characterized them by EI mass spectrometry, IR and ^{19}F NMR spectroscopy (both 1 D and 2 D). Comparison with data for mono-oxides and the observed lack of connectivity between the fluorines attached to carbons adjacent to oxygen, indicate that these compounds are diethers with oxygen inserted between fluorinated carbons. Structures proposed on the basis of the NMR spectra and semiempirical calculations are found to be consistent with HPLC retention times.

Recently, we reported the isolation and characterisation of the first oxahomofullerenes, consisting of three mono-ethers (**A**, **B**, **C**) derived from $C_{60}F_{18}$: calculations correctly predicted that these are the most stable oxide derivatives.[1] The retention times on a Cosmosil Buckyprep column operated under standard conditions (see Experimental section) for **A**, **B** and **C** were 44, 48 and 58 min (Chart 1). Isomer **C** was calculated to be the most stable, and was obtained in by far the largest yield (*ca.* 30 times more than each of the other two).



A, 44 min

B, 48 min

C, 58 min

Chart 1 Ethers $C_{60}F_{18}O$, **A**, **B** and **C**, and their HPLC retention times. The numbering in **B** relates to the NMR peak assignments of Fig. 2a. Fluorine addends are indicated by ●.

The oxahomofullerenes are the oxygen analogues of the nitrogen-containing azahomofullerenes, many of which have been synthesised;[2] a number of bis(azahomo)fullerenes are also known.[3] We have now isolated the first diethers (bis(oxahomo)-fullerenes), and deduced their structures based on analysis of their ^{19}F NMR spectra (both 1 D and 2 D), their retention times during HPLC (high pressure liquid chromatography) separation, and calculations of relative energies.

Experimental

[60]Fullerene (240 mg) was ground in a dry box with K_2PtF_6 (575 mg) and heated to 465 °C at *ca.* 0.01 bar in a glass tube contained within a furnace.[4] The crude fluorofullerene mixture (300 mg, 85%) was partly pre-purified by vacuum sublimation and a sample (*ca.* 280 mg) was dissolved in dry toluene (25 ml) and filtered under conditions which avoided moisture condensation. Purification by HPLC, (10 mm × 250 mm Cosmosil Buckyprep column) with toluene elution at a flow rate of 4.7 ml min^{-1} yielded, together with recovered [60]fullerene (*ca.* 75 mg), $C_{60}F_{18}$[5] (*ca.* 100 mg), and a number of other components. Dioxide derivatives, $C_{60}F_{18}O_2$, were isolated with retention times of 52, 55, 63.3, 64.6, 67.4 and 85 min. All samples gave a peak at 1094 amu, and a typical plot is shown in Fig. 1. ^{19}F NMR spectra were run at 338.9 MHz.

Results and discussion

Our analysis of the structures is based on a combination of retention times *vs.* those for the mono-ethers, the relative yields of the mono-ethers, symmetry of the products, the ^{19}F NMR spectra (both 1 D and 2 D), and calculated heats of formation (see Appendix for details). We suggest that the dioxides that contain the ether motifs **A**, **B**, or **C** will have *approximately* increasing retention times along that series. With regard to yields, since the isomer **C** occurs with the highest yield in the mono-oxides, one could expect that dioxide isomers possessing this motif will be predominant. The ^{19}F NMR spectra will show either ten lines (8×2 F + 2×1 F) if the compound is symmetrical (*i.e.* has C_s symmetry) or 18×1 F if it is not. Minor symmetry is possible only for pairings of the same motif, and in fact is forced for **C** + **C**.

52 min sample (isomer 1)

This was obtained as a mixture together with a component of 1128 amu which, from the mass spectrum fragmentation pattern, we attribute to $C_{60}F_{17}OCF_3$. The sample was

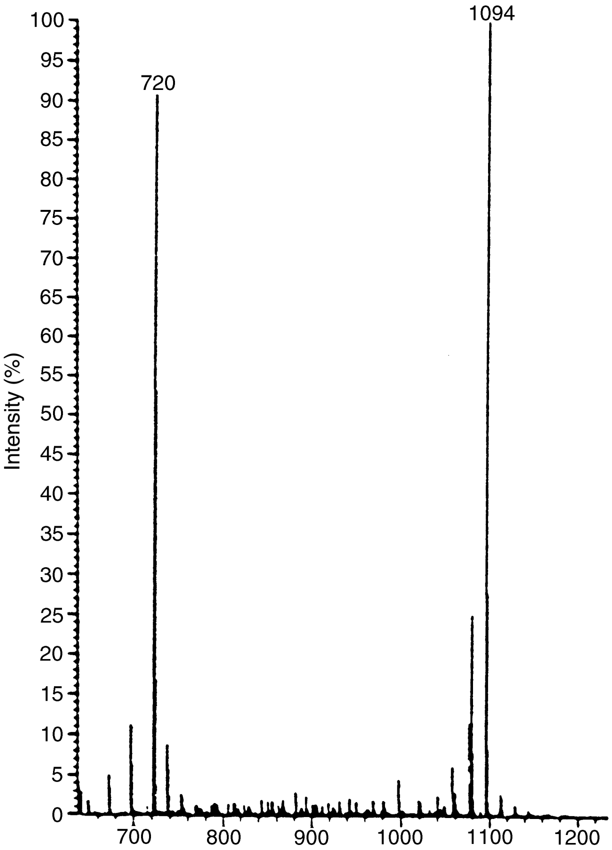


Fig. 1 EI mass spectrum (70 eV) for $C_{60}F_{18}O_2$; all other isomers gave similar mass spectra.

reprocessed into four fractions in the hope that by different measurements, and comparison with the mass spectra for each fraction, the appropriate peaks could be identified. Unfortunately the fraction with the longest elution time, and which contained the highest relative amount of $C_{60}F_{18}O_2$ was obtained in very low yield; its ^{19}F NMR spectrum consisted of *ca.* eighteen lines and so the structure is likely to be unsymmetrical.

The ^{19}F NMR spectrum of **1** contains two downfield peaks at δ_F −78 and −79.3, and two at −91.2 and −116.5. Recall that the most downfield peaks in the most rapidly eluting mono-ether **A** appeared at δ_F −74.6 and −77.9, whilst for **B** they appeared at −91.6 and −115.8.[1] The shifts suggest that **1** should contain motifs **A** and **B**, though the rapidity of elution suggests that **A** + **A** combinations should perhaps be considered also. In fact **A** + **A** combinations are ruled out directly by the NMR data: there are four possible structures involving all possible combinations of the motif present in **A**, *viz.* **1a**–**d**, of which **1a**,**b**,**d** are symmetrical and **1c** unsymmetrical. The former trio require only ten lines, and **1c** requires four peaks in the −80 ppm region, instead of the observed two. All four isomers are also of relatively high energy for diethers, according to AM1 calculations (Table 1). A more likely possibility for **1** is therefore a combination of an **A** and a **B** motif. This gives six possibilities **1e**–**j**, of which one (**1e**) has oxygen inserted into adjacent C–C bonds. All are unsymmetrical and have similar calculated energies, with AM1 finding five isomers within a range of 5 kJ mol^{-1}. With the data available, no further assignment is possible.

55 min sample (isomers 2 and 3)

The mass spectrum for this component showed a single line at 1094 amu. In the IR spectrum (KBr), bands were found at 1206, 1170, 1150, 1135, 1114 (main), 1066, 1049, 938 and 564 cm^{-1}.

The ^{19}F NMR spectrum for this sample (Fig. 2b) consists of 27 lines [peaks marked x are due to a small amount of mono-ether **C** which has a similar retention time]. Hence this component is interpreted as a mixture of two compounds, one symmetrical, the other unsymmetrical (with one coincidence). There are *three* peaks in the −90 ppm region (all dd at δ_F −88.7, −89.8, and −91.1), *three* in the −115 ppm region (at δ_F −115.0, −115.6, −117.1), and *three* in the −127 ppm region. Fig. 2a is the spectrum obtained previously for mono-ether **B**, and shows a *single* peak in each of these (−90, −115, and −127 ppm) regions. Moreover, the other groups of peaks in Figs. 2a and 2b show similarities in location. It is probable therefore that the two isomers each contain a combination of two **B** motifs. There are three possibilities for non-adjacent insertion of this type, **2a**–**c**, of which **2a** and **2c** are symmetrical. Adjacent insertion as in **2d** is energetically unfavorable by ~40 kJ mol^{-1} (at least one of the C–F or C–O bonds must point into the cage) and would lead to a markedly downfield resonance in the NMR spectrum due to the oxygen-flanked C–F bond, which is not seen. Thus the product is likely to consist of a mixture of **2b** with either **2a** or **2c** (the calculations favour the former pair), each predicting a 10 + 18-line spectrum.

A notable feature of the 2 D ^{19}F NMR spectrum (Fig. 3) is that the integrated peak heights (not shown) are mostly identical. This indicates that the symmetrical isomer is present in half the quantity of the unsymmetrical isomer, consistent with the 2 : 1 ratio of the group orders, and the near equality of the isomer energies (see Table 1). To interpret the spectrum, we recall the assignments of the 1 D spectrum (Fig. 2a) of the mono-ether **B** and relate them with the position labels appearing in **B**. The 2 D ^{19}F NMR spectrum for the 55 min sample (isomers **2** and **3**) is shown in Fig. 3.

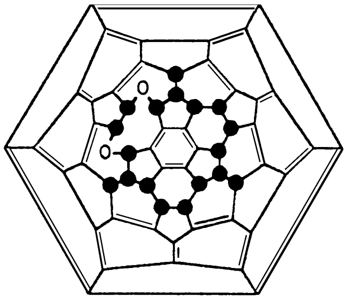
In the unsymmetrical isomer there will be two downfield positions (corresponding to mono-oxide peak 1), and these will be coupled to two of the most upfield peaks (corresponding to mono-oxide peak 17). For the symmetrical isomer there will likewise be one downfield peak with coupling to one upfield peak; these patterns are evident in Fig. 3. Further upfield, there will be two peak pairs at *ca.* −115 and −127 ppm (corresponding to peaks 2 and 3) for the unsymmetrical isomer, and one corresponding peak in each region for the symmetrical isomer. By contrast, whereas there are two fluorines giving rise to peaks 4 and 5 in the mono-ether, there is only one fluorine in a comparable location in each of the diether isomers, and hence only a single peak for each isomer is observed in this region of the spectrum, and the multiplicities seen further downfield in the mono-ether spectrum are likewise absent. Further analysis of the 2 D spectrum is not possible because of coincidence of some peaks, but there is a measure of consistency in our analysis as for example there are no connections within the groups of triplets.

63.3 min sample (isomer 4)

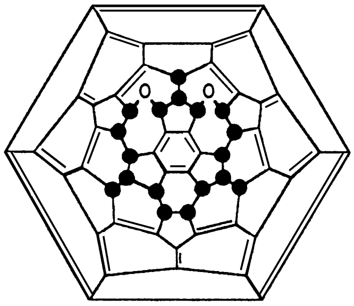
This fraction co-eluted initially with the following fraction and careful reprocessing was needed in order to separate them. The mass spectrum again gave a single peak of 1094 amu, and the IR spectrum (KBr) showed bands at 1218, 1186, 1164, 1131 (main), 1101 and 1067 cm^{-1}.

The ^{19}F NMR spectrum (Fig. 4) consists of eighteen lines at δ −75.4, −80.1, −95.3, −97.1, −129.1, −134.3 (2 F), −134.9, −137.7, −138.2, −150.8, −151.1, −151.9, −153.9, −160.4, −166.3, −169.8, −170.9. The two lines at −75.4 and −80.1 ppm indicate the presence of motif **A** (in mono-ether **A** the lines appeared at −74.6 and −83.8 ppm), and the two downfield lines at δ −95.3 and −97.1 correspond to the most downfield line at −94.6 ppm for isomer **C**.

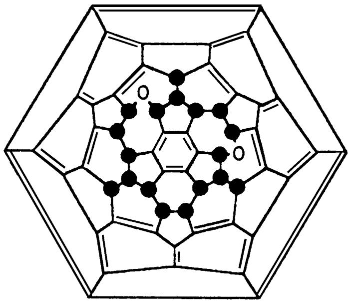
It is likely therefore that isomer **4** contains both **A** and **C** oxygens, two lines being obtained for the **C** site because of the symmetry breaking. There are two possible structures, **4a**,**b**,



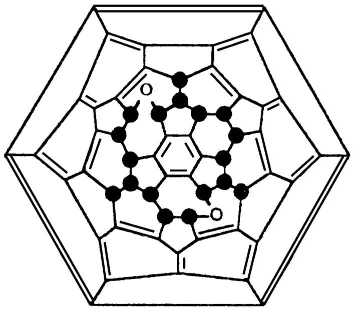
1a



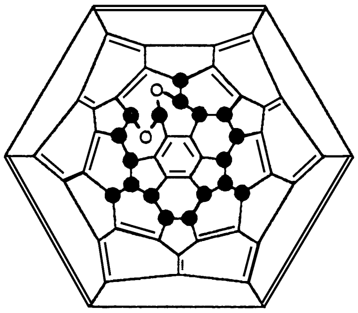
1b



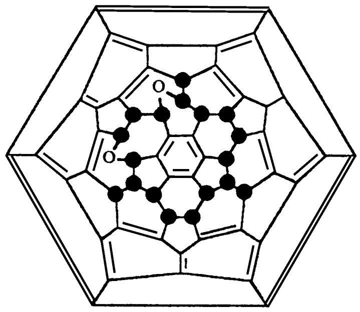
1c



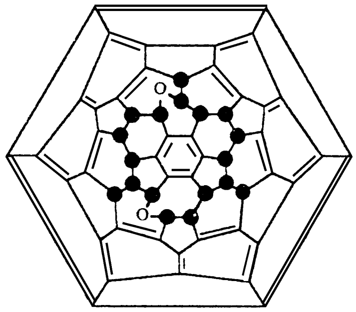
1d



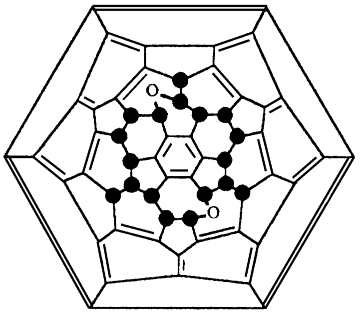
1e



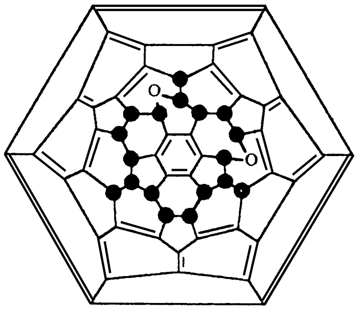
1f



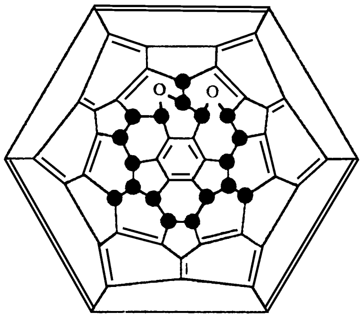
1g



1h



1i



1j

assuming that the two oxygens are not adjacent (**4c**) (since this would exhibit a far-downfield peak). The spectrum shows the characteristics of both mono-ethers **A** and **C**, in having a group of lines in the −127 to −137, −150 to −155, and −160 to −170 ppm regions. For **A** these are at −127.7, −132.7, −134.2, −135.1, −137.5, −138.5, −146.1, −146.4, −146.6, −146.8, −149.2, −160.8, −163.3, −170.1 and for **C**, −132.9, −133.1, −137.6, −138.4, −147.6, −148.2, −151.0, −161.3 and −168.8. Because the amount of this isomer was small, it was not possible to obtain a 2 D ^{19}F NMR spectrum. All three isomers **4a–c** are of similar calculated energy (Table 1).

64.6 min sample (isomer 5)

This fraction was isolated from the preceding isomer by careful reprocessing of the initially-separated sample. The mass spectrum gave a single peak of 1094 amu, and the IR spectrum (KBr) was almost identical to that for isomer **4**, showing bands at 1237, 1218, 1186, 1164, 1131 (main), 1102, 1069 and 1061 cm^{-1}.

The ^{19}F NMR spectrum (Fig. 5) consists of eighteen lines at δ −89.2, −93.0, −101.7, −115.4, −124.2, −133.7, −134.4, −137.5, −137.9, −140.6, −147.2, −150.9, −151.2, −154.3,

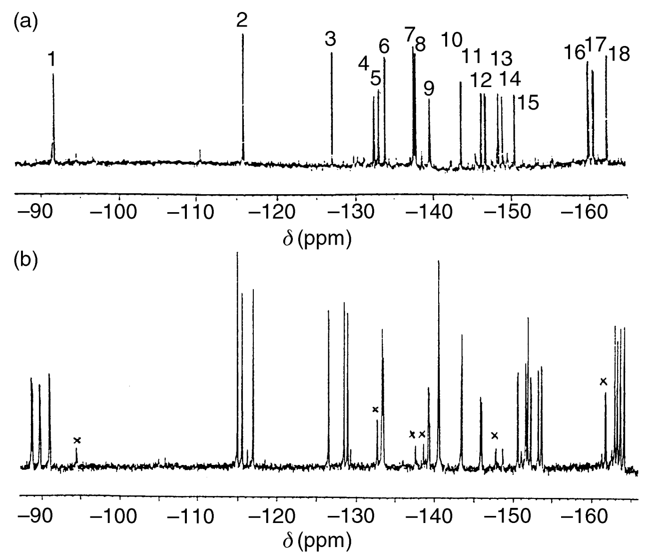
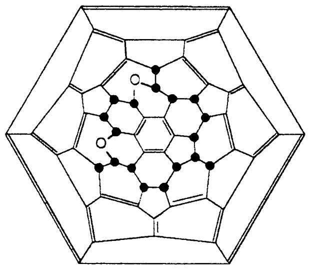
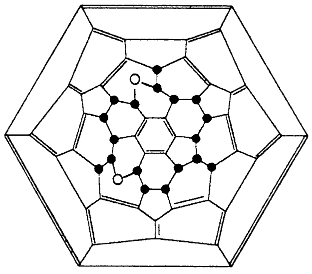


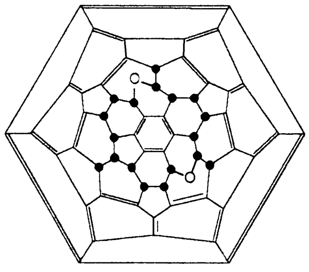
Fig. 2 (a) ^{19}F NMR spectrum for **2**/**3** (x = peaks due to mono-oxide—see text); (b) spectrum for the mono-ether **B**, showing the similarities in the peak positions.



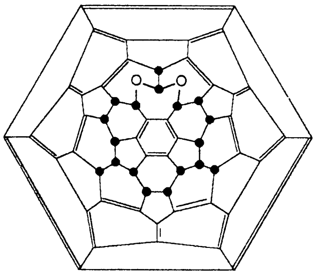
2a



2b



2c



2d

−157.4, −163.3, −164.5, −171.4 (minor lines are due to traces of the isomer **4**). Given that mono-ether **B** gives downfield lines at −91.6 and −115.8, and **C** gives a line at −94.6, then a combination of these motifs (together with symmetry breaking) should give four peaks in the −90 to −115 region, as observed. There are three possible isomers, **5a**–**c**, but these are not fully distinguished by the 2 D ^{19}F NMR spectrum (Fig. 6), because not all of the expected connections are shown, a common problem when experimenting with low sample quantities. Nevertheless, the peaks labelled in **5b** are consistent with the connections evident on the 2 D spectrum. Isomers **5a** and **5b** are predicted to be isoenergetic and are amongst the most stable candidates in the AM1 model (Table 1).

67.4 min sample (isomer 6)

The mass spectrum of this fraction gave a single peak of 1094 amu (not shown). The IR spectrum (KBr) was noticeably more complex than that of the other isomers, showing bands at 1235, 1218, 1214, 1189, 1164, 1143, 1130, 1115, 1102, 1086, 1062, 1058 (main), 1030, 941, 862, 844 and 733 cm^{-1}.

The ^{19}F NMR spectrum (Fig. 7a) consists of eighteen lines at −92.3, −96.5, −96.7, −116.6, −128.9, −133.7, −134.4, −140.2, −145.0, −151.0, −151.7, −152.9, −153.6, −164.5,

Table 1 Relative energies of isomers of $C_{60}F_{18}O_2$, calculated as differences (with **C** + **C**) in AM1 heats of formation (kJ mol^{-1}). All distinct pairing of motifs **A**, **B**, **C** are listed

Type	(a,b) (c,d)[b]	Isomer	Symmetry	ΔE_{AM1}/ kJ mol^{-1}
A + **A**	(1,2) (3,4)	**1a**	C_s	185.6
A + **A**	(1,2) (8,24)	**1b**	C_s	207.9
A + **A**	(1,2) (18,36)	**1c**	C_1	188.1
A + **A**	(1,2) (37,38)	**1d**	C_s	201.3
A + **B**	(1,2) (1,9)	**1e**	C_1	124.4
A + **B**	(1,2) (4,17)	**1f**	C_1	123.1
A + **B**	(1,2) (22,39)	**1g**	C_1	128.7
A + **B**	(1,2) (38,39)	**1h**	C_1	124.3
A + **B**	(1,2) (17,18)	**1i**	C_1	147.2
A + **B**	(1,2) (8,9)	**1j**	C_1	125.3
B + **B**	(1,9) (4,17)	**2a**	C_s	61.3
B + **B**	(1,9) (17,18)	**2b**	C_1	65.7
B + **B**	(1,9) (38,39)	**2c**	C_s	72.7
B + **B**	(1,9) (8,9)	**2d**	C_s	107.9
A + **C**	(1,2) (23,24)	**4a**	C_1	93.2
A + **C**	(1,2) (36,37)	**4b**	C_1	96.5
A + **C**	(1,2) (2,3)	**4c**	C_1	90.6
B + **C**	(1,9) (2,3)	**5a**	C_1	54.1
B + **C**	(1,9) (3,14)	**5b**	C_1	54.1
B + **C**	(1,9) (36,37)	**5c**	C_1	28.2
C + **C**	(2,3) (23,24)	**7**	C_s	0.0
[a]	(1,9) (10,11)	—	C_1	63.4
[a]	(1,9) (15,16)	—	C_1	63.5
[a]	(2,3) (40,41)	—	C_1	88.8
[a]	(2,3) (9,10)	—	C_1	110.3
[a]	(2,3) (39,40)	—	C_s	116.4

[a] See text. [b] Numbers in parentheses refer to the locations of the inserted oxygens; $C_{60}F_{18}$ has fluorines on sites 1–4, 8–19, 16–18, 22–24 and 36–40 in the standard IUPAC labelling.

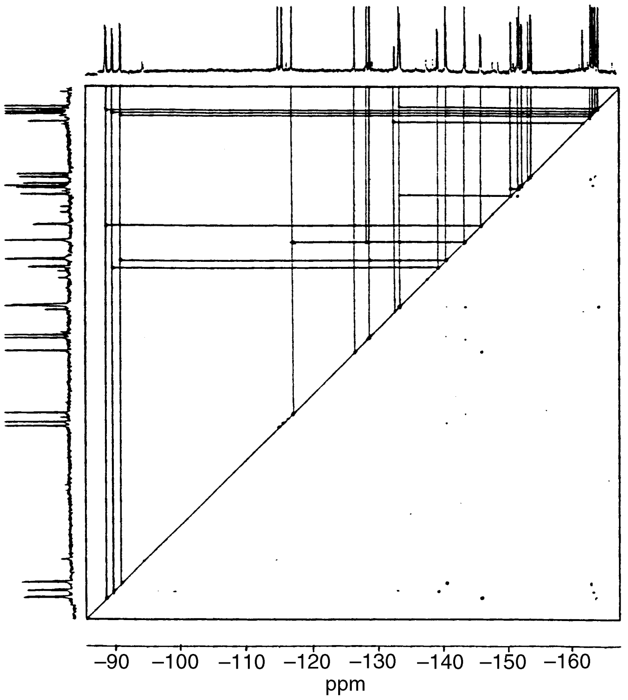


Fig. 3 2 D ^{19}F NMR spectrum for **2**/**3**.

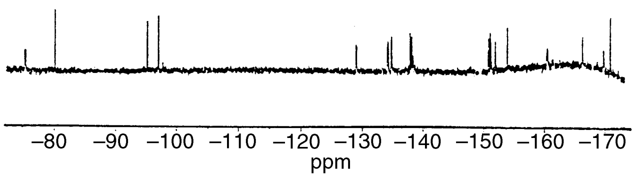


Fig. 4 ^{19}F NMR spectrum for **4**.

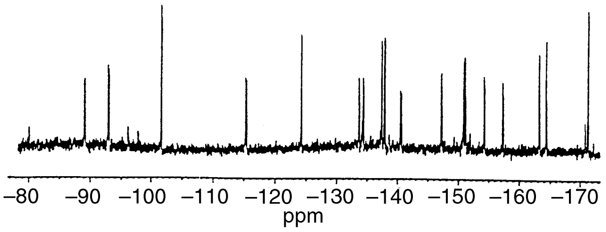
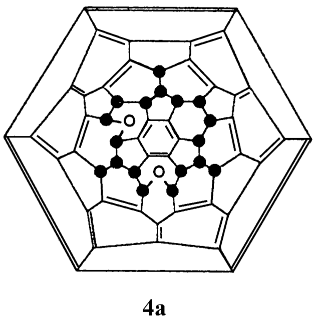
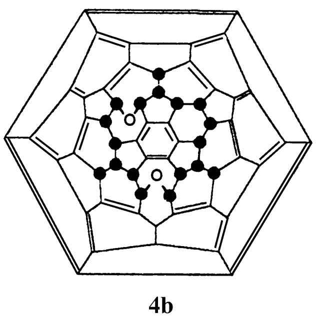


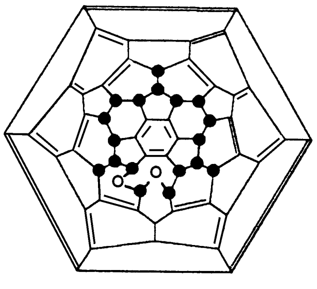
Fig. 5 ^{19}F NMR spectrum for **5**.



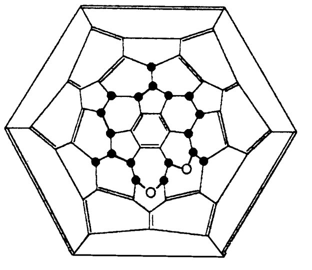
4a



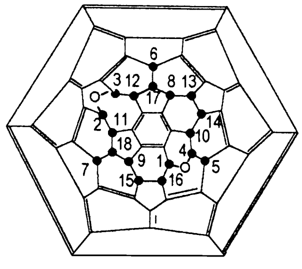
4b



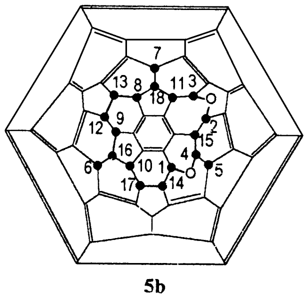
4c



5a



5c



5b

−169.6, −171.9 ppm. The positions of the four most-downfield peaks show that this isomer, like **5**, contains the motifs present in the mono-ethers **B** and **C**. However, here the splitting of the peak at −94.6 ppm in mono-ether **C**, is only 0.2 ppm, compared to 12.5 ppm in isomer **5**. Moreover the peaks which appear at −91.6 and −115.8 ppm in mono-ether **B**, are only perturbed by 0.8 ppm. This suggests that the two oxygen functions are well separated, and are furthermore close to the symmetry plane that would bisect the C–O–C bond equivalent to that present in mono-ether **C**. This identifies isomer **6** as structure **5c**. Furthermore, structure **5c** is predicted to have a significantly lower energy than the other **B** + **C** candidates (by ~ 25 kJ mol^{-1} in the AM1 model).

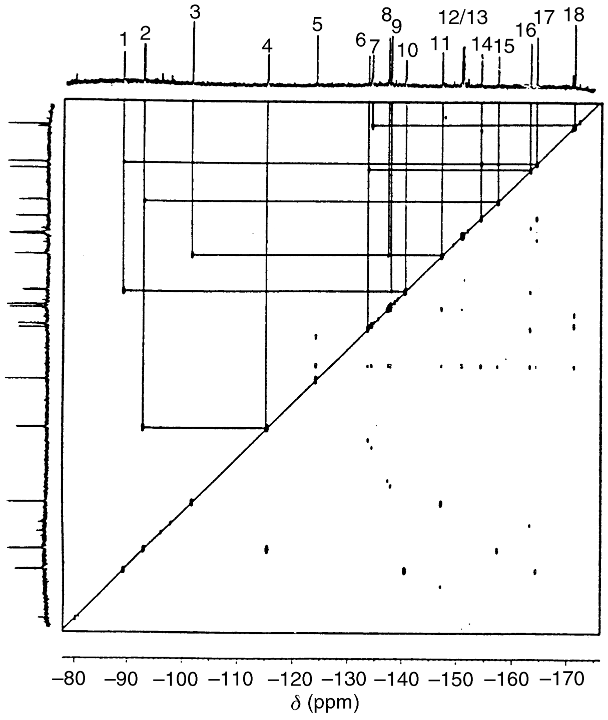


Fig. 6 2 D ^{19}F NMR spectrum for **5**.

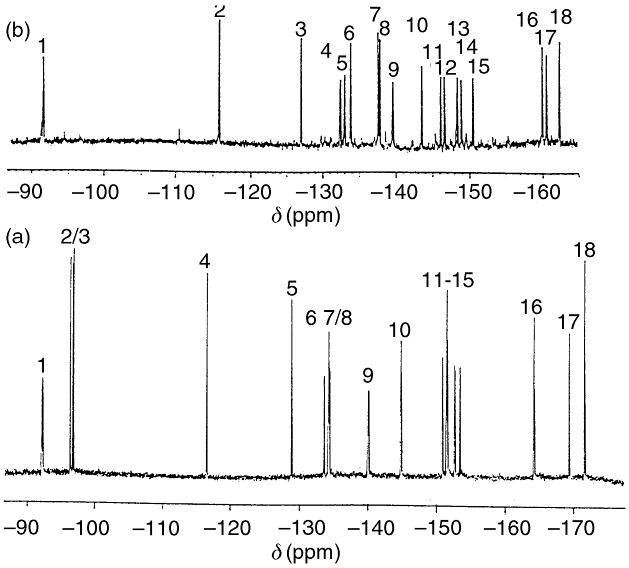


Fig. 7 (a) ^{19}F NMR spectrum for **6**; (b) spectrum for mono-ether **B**.

A notable feature is that the spectrum shows considerable similarity with that for the mono-ether **B** (Fig. 7b), the main difference being that peaks 7 and 8 in the mono-ether have become peaks 2 and 3 in the bis-ether. As a result, peaks 2–6 in the mono-ether correspond to peaks 4–8 in the diether (compare Figs. 7a and 7b); the clusters 11–15 and 16–18 in each spectrum clearly relate to fluorines in similar environments in each molecule. Moreover, from the 2 D ^{19}F NMR spectrum (Fig. 8), it is seen that the strong couplings in the mono-ether, *viz.* 18–5, 17–1, 16–4, 10–2,3 and 9–1[1] are the same in the diether *viz.* 18–7, 16–1, 17–6, 10–4,5, and 9–1 (after allowing for the peak number changes described above); perturbation by the second oxygen may account for the connection 17–1 in the mono-ether becoming 16–1 in the diether.

The downfield shift of peaks 7 and 8 in the mono-ether to 2 and 3 in the diether allows unambiguous identification of the

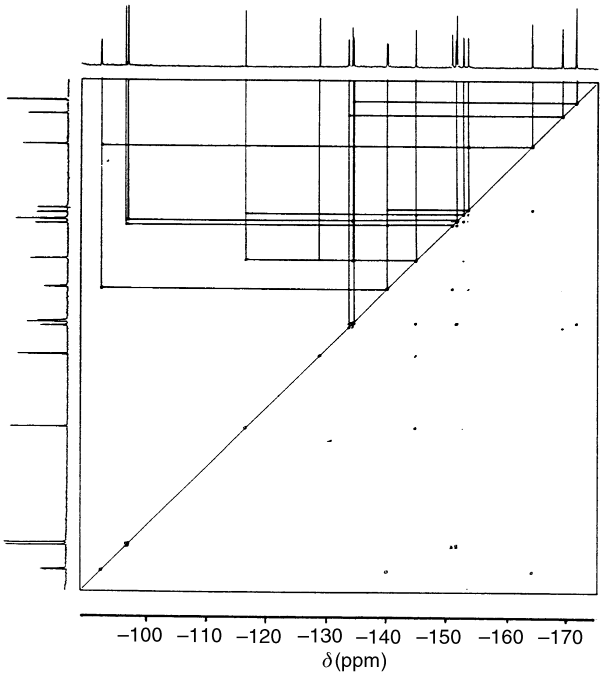


Fig. 8 2 D ^{19}F NMR spectrum for **6**.

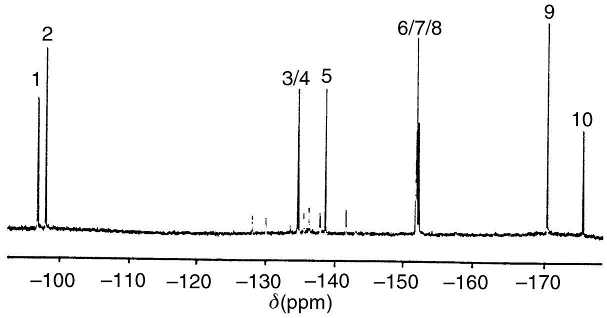


Fig. 9 ^{19}F NMR spectrum for **7**.

fluorines in the former as the pair between which oxygen inserts. This aided the assignments in mono-ether **B**.[1]

85 min sample (isomer 7)

The fraction obtained from the initial HPLC separation was a mixture. Re-separation yielded an initial fraction of 84 min retention time, which consisted of a mixture of $C_{60}F_{16}$[6] and $C_{60}F_{20}O_2$ (1132 amu). The tail fraction gave a peak at 1094 amu, but was not entirely free from the minor oxide components, $C_{60}F_{18}O_3$ (1110 amu) and $C_{60}F_{20}O_3$ (1148 amu), which show up as minor peaks in the ^{19}F NMR spectrum. The IR spectrum (KBr) bands showed just three bands at 1159/1155, 1130 (main), and 1091 cm^{-1}, indicative of a symmetrical structure.

The ^{19}F NMR spectrum (Fig. 9) consists of just ten lines at δ_F −96.9 (2 F), −98.1 (2 F), −134.77 (1 F), −134.82 (2 F), −138.7 (2 F), −151.91 (2 F), −152.03 (2 F), −152.25 (2 F), −171.1 (2 F), −176.4 (1 F). Thus this isomer is symmetrical and the appearance of two lines in the −97 ppm region indicates the presence of the oxygen motif of the mono-ether **C** with a splitting into two lines because the local symmetry across each C–O–C bond is lost. There is one possible structure **7**, and it is confirmed by the 2 D ^{19}F NMR spectrum (Fig. 10). From the spectrum alone, it is not possible to distinguish between positions 1 and 2, or between positions 7 and 8 in the assignment.

Isomer **7**, with its unique **C** + **C** pattern, is predicted by AM1 to be the most stable diether and hence the most stable of all the

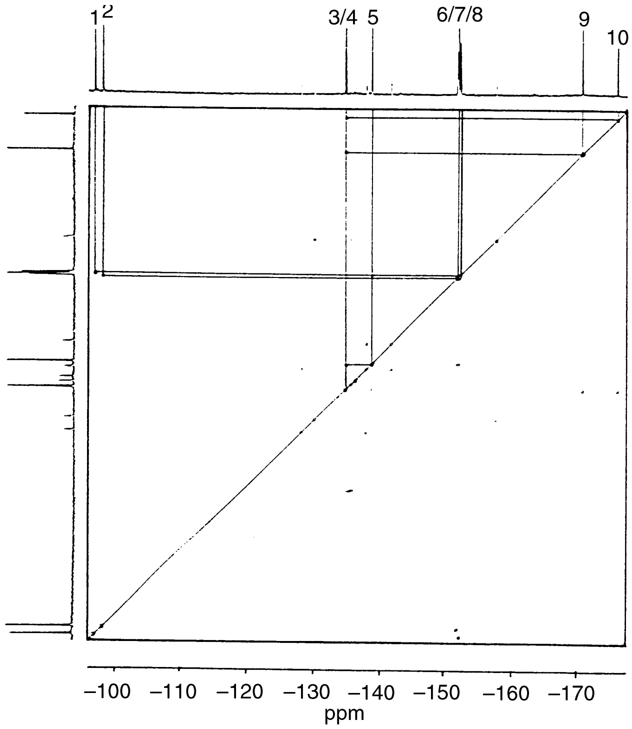
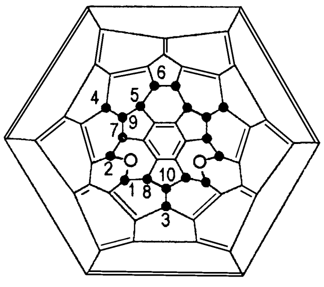


Fig. 10 2 D ^{19}F NMR spectrum for **7**.



7

bis(oxahomo) derivatives of $C_{60}F_{18}$ (Table 1). This correlates with the prediction that **C** is the most stable of the mono-ethers and supports an additive model of stability.

Elution order

There is very good consistency in the elution order for these diethers compared to those for the mono-ethers, which eluted in the order **A** < **B** < **C**. A simple combination of the elution times would predict the order for the diethers containing these mono-ether motifs as **A** + **A**, **A** + **B**, **B** + **B**, **A** + **C**, **B** + **C** and **C** + **C**. Apart from the lack of any isolated **A** + **A** isomer, this is almost precisely the order which we obtain, *viz.*: **1**, **A** + **B**; **2** and **3**, **B** + **B** (both); **4**, **A** + **C**; **5**, **B** + **C**; **6**, **B** + **C**; **7**, **C** + **C**. This further supports the identification of the structures in the foregoing discussion. It is interesting to note that the calculated stabilities follow the same order (**A** < **B** < **C**) as the retention times for mono-ethers and that additivity is also good guide to the stabilities of the diethers. An obvious conjecture is that the observed minor component $C_{60}F_{18}O_3$ would have the C_{3v} **C** + **C** + **C** structure. Anticipated calculations of stabilities of **C** + **C** + **C** compared to some **B** + **C** + **C** and **B** + **B** + **C** isomers give structure **C** + **C** + **C** to be ~40 kJ mol^{-1} more stable than its rivals.

Appendix

Optimised structures and heats of formation using the semi-empirical AM1 Hamiltonian were calculated from a set of hypothetical $C_{60}F_{18}O_2$ species. All distinct combinations of oxygen insertions into or additions across C–C bonds of the C_{3v} $C_{60}F_{18}$ structure were considered, apart from those including the six bonds of the benzene ring in the crown. The total number of candidate structures was 608. These include all diethers combinations of motifs **A**, **B** and **C**, but also many other structures, *e.g.* diepoxides and mixed ether–epoxides. The calculated heats of formation span a large range (at least 580 kJ mol^{-1}), but as expected from previous experience with the mono-oxahomo species, all the most stable structures are of a diether type (see Table 1). This general preference, but not necessarily the precise order of isomer energies, is expected to be robust against changes in method of calculations, as MNDO and AM1 heats of formation for the mono-oxygen species have already shown a good correlation.[2] Calculations were not repeated with MNDO and PM3 for all 608 isomers, but for the subset of diethers all three methods are indeed found to be in agreement.

At the AM1 level, the isomer of minimum energy is **7**, with a calculated heat of formation at −557 kJ mol^{-1}, and the next most stable is **5c**, at −528 kJ mol^{-1}. The relative stabilities of all isomers considered above are listed in Table 1; included in Table 1 are data for some other low energy isomers involving addition across the 9,10-bond (which is not found with either the mono- or diethers, due presumably to kinetic effects).

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